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Lead Sulphide-Doped Silica Xerogel by Sol-gel Technique

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ABSTRACT

In this paper, a chemical process based on using sol-gel technique for the preparation of microcrystalline *PbS*-doped silica xerogel is described. Compared with the absorption spectra of bulk *PbS* crystals, the absorption edges of microcrystalline *PbS*-containing material exhibit large blue shift, due to confinement of microfine *PbS* particles in silica matrix. Because of the non-linear properties, this xerogel finds use in photonics as a cut-off filter.

1. INTRODUCTION

The materials with high third-order nonlinearity are of great interest for photonic application due to intensity-dependent refractive index of these materials. Such a material has been reported by incorporating microcrystalline dots of semiconductor, such as *CuCl*, *CdS*, *CdSSe*, etc. in glasses, e.g., silica glass and sodium borosilicate glass¹⁻³. Sol-gel technique in its variation offers a process for preparing such materials⁴.

In this paper, a process based on sol-gel technique for the preparation of microcrystalline *PbS*-doped silica xerogel is described.

2. EXPERIMENTAL DETAILS

Several materials were used in the preparation, which include tetraethylorthosilicate (TEOS) as a source of silica, methanol (A.R. grade) as a solvent, nitric acid (A.R. grade) as a catalyst, lead acetate and saturated *H*₂*S* water solution as a source of *PbS*, and double distilled water.

For the preparation of microcrystalline *PbS*-doped silica gel, first 10.4 g TEOS was hydrolysed by mixing with equal volume of methanol and 1.8 ml of 0.15 N

*HNO*₃ solution for 1 h. To this solution, 15 ml methanolic solution of lead acetate was added. The mixture was stirred for 3 h. Finally, a mixture of 4 ml methanol + 1.5 ml of 0.15 N *NH*₄*OH* was added to adjust pH of sol to ~ 5. Uniform colourless sol was obtained at this stage. No reflexing of sol is required. The gels were cast in polythene petri dish. Gelation took place in 3 to 4 h. Colourless transparent gels were obtained. Two-stage hydrolysis—first acidic then alkaline—helped in obtaining colourless transparent gels rapidly. In the first stage during acid treatment, the condition was favourable for quick hydrolysis of alkoxy groups. In the second stage during alkaline treatment, the condition favoured fast condensation reaction. The high condensation rate in second stage also helped in drying the gel without fracture.

The gels were allowed to dry at room temperature for 24 h. Next day, the gels were immersed in saturated *H*₂*S* water solution for 24 h. After this, the gels were washed with distilled water and dried at 110 °C. Quantity of *PbS* in the xerogel was varied by adding calculated volume of lead acetate solution of known strength.

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The xerogel obtained was investigated for its structure by X-ray diffraction measurements with Philips X-ray diffractometer, using monochromatic $\text{CuK}\alpha$ radiation. Optical absorption spectra were measured on 0.5 mm thick xerogel with Cary 17 D spectrophotometer.

3. RESULTS & DISCUSSION

Results of the X-ray diffraction patterns of xerogel are presented in Fig. 1 and absorption spectra are shown in Fig. 2.

Lead sulphide content in xerogels varies from 0.1 to 2.4 wt %.

The extent of colouration of the xerogels depends on the quantity of PbS in it, the colour being darker at higher content of PbS .

3.1 Effect of Treatment with Saturated H_2S Water on the Gel

Before treatment with H_2S water solution, the gels were transparent, but they shrank to some extent due to the loss of solvent and water in 24 h. At this stage, two kinds of groups exist on the surface of gel-alkoxy and hydroxyl groups. The treatment with H_2S appears to meet the following objectives:

- (a) The H_2S water diffuses into pores and reacts with the Pb ions to form PbS precipitate in it.

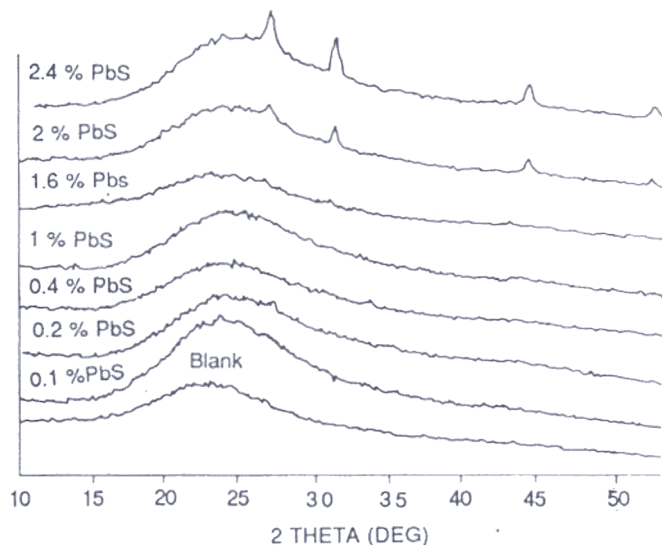
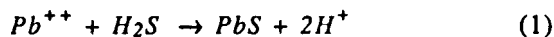


Figure 1. X-ray diffraction patterns of silica gel containing PbS and dried.

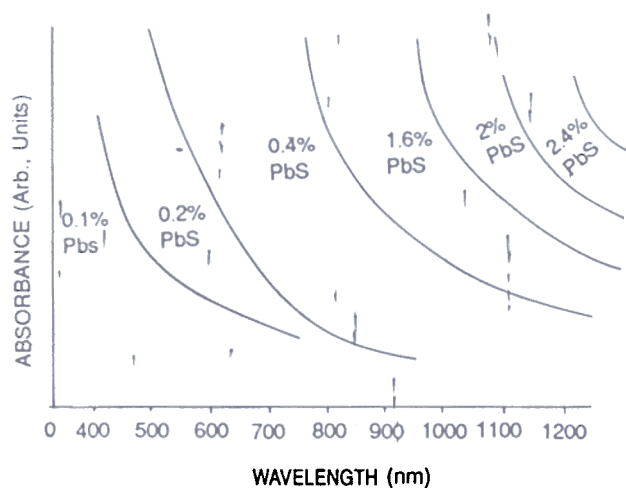
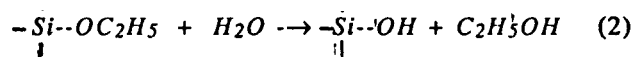


Figure 2. Optical absorption spectra of dried silica-gel containing PbS (The absorption edge for bulk PbS crystal is approximately 3020 nm and is not shown in the figure).

The quantity of PbS in the gel depends on the amount of lead acetate added at the initial stage in the sol.

- (b) Water, on diffusion into pores, reacts with the residual alkoxy groups present in the gel and converts them into hydroxyl groups, thus increasing the number of hydroxyl groups on the surface of the particles by removing alkoxy groups from the gel, according to Eqn (2)



By applying this treatment, the gel could be dried very quickly while maintaining the shape⁵.

Since alkoxy groups were also removed by this treatment, no heat treatment was required for removing these groups from the gel.

From the results of X-ray diffraction (Fig. 1), it was observed that the peaks at $2\theta = 26^\circ, 36^\circ, 43^\circ, 51^\circ$, and 53° , closely resemble those of cubic PbS crystals. The intensity of peaks varies with the content of PbS in the gels. When PbS content is very low, i.e. $<1.6\%$ in the gel, the peaks could not be seen in X-ray curve due to limitation of the instrument.

From the results of absorption spectra (Fig. 2), it was observed that, when compared with the absorption spectra of bulk PbS crystals, the absorption edges on PbS -containing materials exhibit large blue shift because of confinement of fine PbS particles in silica matrix. The particles behave as quantum dots. As the quantity of PbS increases in silica xerogel, the

absorption edge shifts towards bulk PbS crystal which is approximately 3020 nm.

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REFERENCES

1. Schmitt-Rink, S.; Müller, D.A. & Chemla, D.S. Theory of the linear and non-linear properties of semiconductor microcrystallites. *Phys. Rev. B.*, 1987, 35, 8113-25.
2. Jain, R.K. & Lind, R.C. Degenerate four-wave mixing in semiconductor - doped glasses. *J. Opt. Soc. Am.*, 1983, 73, 647-57.
3. Butcher, P.N. & Cotter, D. The optical properties artificial materials. *In* The elements of non-linear optics. Cambridge University Press, Cambridge, 1990, pp. 275-94.
4. Nogami, M.; Walabe, M. & Nagasaka, K. Preparation of semiconducting sulphides microcrystalline - doped silica glasses by the sol gel process. *SPIE, sol-gel optics*, 1990, 1328, 119-24.
5. Minsume, T.; Nagata, H. & Manaba, S. Attempts to avoid cracks during drying. *J. Non-Cryst. Solids*, 1988, 100, 239-40.